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TITLE OF THE INVENTION (280 characters max)

LABORATORY PREPARATION OF LIGHT VALVE SAMPLES

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Respectfully submitted,

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LABORATORY PREPARATION OF LIGHT VALVE SAMPLES

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INTRODUCTION

Thermally activated light valves may be prepared as a layered structure consisting of two transparent cover sheets, such as glass or plastic, with a layer of optically active material sandwiched between the cover layers. This optically active layer may consist of a polymer solution where the polymer reversibly precipitates upon heating to the critical or "switching" temperature for this particular polymer/solvent pair (see US patents 3,953,110 and 5,377,042, by author). The finely divided polymer precipitate has a different refractive index than the solvent, and thus the optically active layer turns a highly reflective, opaque white above the switching temperature, but below the switching temperature, the light valve is as transparent and optically perfect as the cover sheets, eg. plate glass.

In order to achieve a particular desired switching temperature for a light valve, it is possible to mix two monomers: one whose polymer switches above the desired temperature, and the other a monomer whose polymer switches below the desired temperature, mixed in the proportions such that the desired switching temperature is achieved. However, if the lower temperature monomer has too low a switching temperature (eg. by being highly solvent phobic), it may not be soluble enough to be of use. The switching temperature of a polymer solution can also be manipulated by changing the solvent. For example, dissolving some inorganic salt in a water solvent will lower the switching temperature of the polymer/solvent solution.

A fairly random copolymer is required for the light valve to switch "sharply", that is, over a small temperature range. The pairs of monomers must have similar polymerization rates and solubility in order for the copolymer that they form to be random. The monomer pair and the crosslinking monomer should all also belong to the same category of monomers, so that the copolymerization is random. For rapid and complete polymerization, monomers with conjugated unsaturation may be preferred. In the event of breakage of one of the cover sheets, the polymerized gel must be non-toxic. Polymerization must be complete, because unpolymerized monomer would render the finished gel toxic.

Interchain bonds between the polymer chains in solution make the light valve's switching not sharp and the temperature of switching a sensitive function of the concentration of the copolymer in the solvent. Thus, if the seal between the two sheets of cover glass is ruptured and solvent evaporates, the switching temperature of the light valve will drift. An example of a monomer pair which fails due to interchain bonding is hydroxyethyl acrylate/hydroxypropyl acrylate. In this case the interchain bonds are hydrogen bonds between the hydroxy groups which are pendant from the polymer chains. These interchain bonds cause a hysteresis in the switching of the light valve, such that the switching temperature on heating is higher than the switching temperature on cooling. This would be useful for holographic computer memories, but is a problem for light valves.

PROBLEMS WITH PREVIOUS PROCEDURES

Previously light valve samples were prepared by filling between two closely spaced sheets of glass with an optically active aqueous polymer solution. In order for the polymer solution to turn from a viscous liquid to a weak solid, or "gel", the polymer was crosslinked after filling by the previous addition of a redox catalyst pair, such as sodium hypophosphite and hydrogen peroxide, and a crosslinking monomer, such as methylene bisacrylamide (MBA). The catalyst creates free radicals, which transfer to the MBA to activate it, and which also abstract hydrogen from the polymer chain, thereby making sites for the MBA to covalently bond to the polymer chain. Since the MBA is bifunctional, it covalently bonds to two polymer chains, thus crosslinking them to form a solid gel, with the polymer chains still in solution. Examples of optically active polymers used for this purpose include poly N vinyl caprolactam, and poly N isopropyl acrylamide, both in aqueous solution.

In order for the optically active layer to have adequate mechanical properties, the polymer concentration must be 30% or greater. A problem with the above polymers is that even when the degree of polymerization is as low as approximately 50, as determined by dialysis, (the lower limit for obtaining adequate crosslinking for gel formation), the viscosity of a 30% polymer aqueous solution is 20,000 centipoise. This high viscosity makes it slow to remove atmospheric oxygen from the polymer solution. When filling the 1 to 3 millimeter thick cavity between the two cover sheets of glass joined together at their edges by a narrow strip of sealant (see Figure 1), this high viscosity prevents a rapid filling operation. If the filling pressure of the polymer solution is increased in order to obtain a reasonable fill time, this high pressure breaks the glass, even when a reinforcing clamp is used. Further, the inner seal adhesion fails, and the polymer solution leaks past the seal near the fill port.

Catalysts for initiating polymerization, or crosslinking, or gelling, or curing, may be unsatisfactory for the following reasons: Ultraviolet light activated photoinitiators do not work with glass cover sheets because glass is not transparent to the wavelengths (typically the mercury emission line at 316 nanometers) required to activate most UV photoinitiators. Visible light activated photoinitiators are unsatisfactory because they are slow and also because their reaction products generally impart to the light valve a yellowing by sunlight. Organic peroxide catalysts generally require accelerators such as organic cobalt or vanadium compounds, with tertiary amine bases. These accelerators generally either themselves yellow in sunlight or cause the polymer to yellow in sunlight. A redox catalyst system of ascorbic acid/hydrogen peroxide exhibits excellent properties except that the ascorbic acid reaction products turn yellow in sunlight. When the ascorbic acid is replaced with a hypophosphite salt as the reducing agent that is used with the hydrogen peroxide oxidizing agent, the yellowing problem is solved, but the time after filling for the solution to gel is extended to 3 hours, which is not satisfactory.

NEW PROCEDURES AND MONOMER SPECIFICATIONS

In order to obtain rapid fill and gel rates, a new approach was initiated. Since a polymer with even a low degree of polymerization is too viscous for rapid filling, filling with an aqueous solution of monomer was tried, so that both the polymer and the crosslinks would be formed together after filling between the cover sheets. Viscosity decreased by a factor of 1,000, which decreased the fill time by a factor of 50.

The N vinyl caprolactam monomer with a water solvent was not suitable for this new process due to its limited solubility in water at room temperature, and also due to its very slow polymerization, which must be driven by harsh conditions. The N isopropyl acrylamide monomer, although it polymerizes rapidly and completely under mild conditions, is also unsuitable for this new process, due to its limited solubility in water (both of these monomers are solids at 20° C). To make this rapid fill and gel procedure possible, monomers must be molecularly designed to fit the procedure, which defines the first two of the Monomer Specifications.

For light valves which switch, for example, within the range of 25 to 30° C, the copolymer/solvent pair is chosen where the copolymer precipitates within that temperature range. However, if the polymer is formed by the polymerization of an unsaturated monomer, as is usually the case, then this vinyl unsaturation will make the monomer slightly more hydrophobic than the polymer, which does not have the unsaturation. This means that the monomer will be less soluble before it is polymerized. This solubility difference makes it difficult to find a monomer which both exhibits precipitation on heating when it is in polymer form, and which is also soluble at temperatures below the precipitation temperature of the polymer. This difficult requirement generally implies that the monomer is a liquid at 20° C below the precipitation temperature of the polymer, thus increasing its heat of solution and solubility.

The polymerization process, occurring in solution, is exothermic, thus heating the monomer solution during polymerization. However, if the polymerization occurs above the switching temperature of the light valve, the optical properties suffer: the switching from clear to white is less sharp; it occurs over a larger temperature range, and there may be a permanent haze when the light valve is in its clear (or transmissive) state. For this reason the monomer solution can be cooled to approximately 20° C (for monomers with conjugated unsaturation) below the switching temperature of the light valve during filling and polymerization/crosslinking.

A desirable monomer pair and solvent for preparing light valves with this rapid procedure must meet all of the following Monomer Specifications:

- The mixed monomers are at least 35% soluble in the solvent at a temperature enough below the switching temperature of the corresponding copolymer/solvent solution that the heat of polymerization does not raise the solution's temperature to the switching temperature.
- Polymerization is rapid, complete, and repeatable.
- Forms a fairly random copolymer which reversibly precipitates from solution upon heating to the desired temperature.
- Has no strong but reversible bonds between the copolymer chains in solution (eg. Hydrogen or solvent phobic bonds), besides the intended irreversible covalent crosslinks, made to form a gel.
- Forms a copolymer which does not react with the solvent, oxygen, or sunlight.
- The copolymer gel, when below its switching temperature, should exhibit high optical quality, without haze or yellowing after accelerated aging and field testing.
- The copolymer gel must be non-toxic.

NEW MATERIALS AND RESULTS

There is a class of monomers, many of whose members satisfy all of the above requirements when they are used with water as the solvent: the N substituted acrylamides (see Figure 2). The general structure for some of these monomers is shown, along with 7 examples of monomers of interest. The subscripts A, B, and C indicate the number of methylene groups in the monomer and their locations (although acrylamide monomers with satisfactory properties can be made without methylene groups, and some monomers which are not acrylamides may satisfy the Monomer Specifications). The sum $A + B + C$ indicates the hydrophobicity of the monomer and the polymer which it forms. A good candidate acrylamide monomer should have $A+B+C$ between 3 and 5 for a light valve switching near 30°C , and should also be liquid at 10°C , which implies that neither A nor B are zero, in order to avoid a polar amide hydrogen, which would raise the melting point of the monomer, as is the case with N isopropyl acrylamide, which melts at 64°C .

The first example monomer, DEA, has a switching temperature of 30.4°C in water (see Figure 3). In order to increase the switching temperature of polymerized DEA, some of the second example monomer, DMA, is substituted for some of the DEA. Figure 3 shows that substituting 1.5% by weight DMA for DEA increases the switching temperature to 33°C . Conversely, in order to lower the switching temperature, some of the third example monomer, TBA, is substituted for some of the DEA. Figure 3 shows that a 2% substitution of TBA decreases the switching temperature to 24.3°C , while 3% TBA lowers the switching temperature to 20.7°C . The TBA does not satisfy all of the Monomer Specifications because its tertiary butyl group is extremely hydrophobic, and thus forms strong hydrophobic interchain bonds. However, although the TBA and the MBA crosslinker are poorly soluble in water, they are adequately soluble in the DEA/water solution because the DEA couples them into solution, due to their similar acrylamide molecular structures. Since not more than 3% TBA is used, its interchain bonding and low solubility are not problems.

The requirement for rapid and complete polymerization and crosslinking of the aqueous monomer solution argues for conjugated unsaturated monomers (such as substituted acrylamides) activated by a redox catalyst system. These catalysts swing into rapid action as soon as the reducing agent solution and the oxidizing agent solution are mixed. A further advantage of most redox catalysts is that the time for the polymerization and crosslinking reactions may be adjusted by adjusting the initial pH of the aqueous monomer solution. A satisfactory redox catalyst system consists of persulphate/metabisulphite. This system and its reaction products (eg. sodium sulfate) exhibit no absorption of solar ultraviolet light, and therefore cause no yellowing of the optical switch in sunlight. Further, a 0.08% solution of sodium sulfate undergoes no reactions with the polymer or the cover sheets. With an initial pH of 8.0, a polymerization, or gel formation, time of 10 minutes is obtained at 10°C . This is a useful gel time because it is as short as is possible, with most of the polymerization still taking place after the 1 minute duration of filling with the monomer solution. If too much polymerization occurs during filling, the switching temperature and other optical properties are not uniform.

The formulation used for the light valve samples shown in Figures 3, 4, and 5 is 35% monomer (consisting of DEA + DMA or TBA) + 0.07% MBA + 0.04% each of sodium persulphate and sodium metabisulphite + 0.07% pentamethyl piperidone, a hindered amine

sunlight stabilizer which harmlessly decomposes free radicals, and then regenerates itself. The optically active gel layer of these samples were 2 millimeters thick.

Figure 4 shows the switching temperature of light valves with different concentrations of copolymer in water, to simulate the effects of a ruptured seal with consequent loss of water. It may be seen that when the polymer concentration changes from 30% to 40%, the switching temperature changes only 0.7°C , which is a satisfactory performance. Figure 5 shows a light valve subjected to accelerated aging at 70°C and 100% relative humidity for 8 weeks. The switching temperature changes only 0.4°C , which is satisfactory.

LABORATORY PROCEDURES

After the two sheets of glass have been cut to size, and their sharp edges removed (called "seaming" the glass), the untinned side of the glass is washed. First the glass is scrubbed in a soap solution, such as 0.5% Alkonox in deionized water. Then the glass is rinsed in deionized water. Next the glass is soaked for 10 minutes in a hydrochloric solution with a pH of 2.0. The purpose of this mild etching is to remove the sodium and calcium ions from near the surface of the glass, so that the polymer may be bonded directly to the more durable silica portion of the glass. Hydrochloric acid is used because both sodium chloride and calcium chloride are soluble in water. Next, the glass is rinsed again, and then dried.

After drying, the glass is coated with a silane coupling agent, which later will covalently bond the polymerizing polymer chains in aqueous solution to the silica surface of the glass. The silane which has been found to work best is vinyl trimethoxy silane, prepared as a 1% solution in methyl alcohol which has been dried with a molecular sieve. The pH of this solution is adjusted to 7.0 with glacial acetic acid. No water is added to this solution to prehydrolyze the silane. The solution is used between two and six hours after it is prepared, with older solutions discarded.

This silane solution may be sprayed onto the glass with an airless spray gun, and with the solution pressurized to 2000 pounds per square inch. Alternately, an air brush may be used. After the silane coating has dried (which is virtually instantaneous), the glass is placed in an oven to covalently bond the silane to the glass. The forced air oven is at 100°C , and the silane coating is cured for 20 minutes.

To fill the glass/cavity/glass sandwich, the monomer solution is injected with a two barreled syringe. It may be preferred to use a 4:1 volume ratio between the two barrels, with the larger barrel called part A and the smaller barrel called part B. The reducer and the oxidizer components of the redox catalyst pair are placed in different barrels, so that when the cartridges are discharged, the two components mix and the polymerization and crosslinking reactions start. It has been found that the sodium persulphate oxidizer should be mixed with the monomer because when the sodium metabisulphite reducing agent is mixed with the monomer, then polymerization starts immediately, even before addition of the sodium persulphate solution.

Part A typically consists of: 42% monomer + 0.08% MBA, + 0.08% pentamethyl piperidone, + 0.05% sodium persulphate, and has a pH of 8.0, adjusted with solutions of sulfuric acid and sodium hydroxide. Part B consists of 0.20% sodium metabisulphite, with the remainder of A and B being enough water to make A:B = 4:1.

Because, as with most free radical polymerizations, oxygen inhibits polymerization by quenching free radicals, parts A and B must have dissolved atmospheric oxygen removed from them before adequate and repeatable polymerization can occur. There are two outgassing procedures for doing this: while parts A and B are in the cartridge, an inert gas, such as nitrogen, argon, or helium, may be bubbled through the solutions A and B for 10 minutes; or the dissolved oxygen may be removed by placing the cartridge in a vacuum and boiling solutions A and B. A boiling chip placed at the bottom of each cartridge cylinder facilitates this out-gassing procedure. Either bubbling with an inert gas or vacuum boiling, or both, may be used.

Immediately when parts A and B leave the two cylinders of the syringe cartridge, they enter a static mixer with 10 mixing elements; this static mixer should have a small diameter to promote turbulence and consequent good mixing of the parts A and B. Poor mixing results in swirl patterns that display the flow patterns of the monomer solution during filling in the polymerized sample when it is close to its switching temperature, which is objectionable. At the end of the static mixer is fastened either a hypodermic needle of large diameter or a filling die.

The unfilled sample, or glass/cavity/glass sandwich, may consist of two sheets of glass joined around their edges by an inner sealant, typically 3/8 inch wide (see Figure 1). When a hypodermic needle is used to fill the sandwich with the mixed parts A and B, it is pushed through the inner sealant. When a die is used for filling, a gap is left in the inner sealant which fits the die precisely to avoid leakage. On the corners of the glass opposite the filling port, hypodermic needles may be inserted through the sealant in order to allow the gas trapped between the two layers of glass to escape during filling with the monomer solution. Before the mixed parts A and B are injected into the sample, the oxygen-containing air between the two sheets of glass must be removed so that it doesn't prevent uniform polymerization. This is done by flushing the cavity in the sample with an inert gas.

In order to prevent the heat of polymerization from switching the sample during polymerization, the glass/cavity/glass sandwich and the syringe containing parts A and B are placed in a 5° C cooler for 15 minutes, and the mixed parts A and B are injected immediately after the unfilled sandwich and syringe are removed from the cooler. Immediately after filling, the filled sandwich is placed back in the cooler. In approximately 10 minutes the polymerization has turned the solution from a liquid to a crosslinked gel.

At this point, the sample may be handled gently and is removed from the cooler. Then the hypodermic vent needles are removed and the holes left by the vent needles and the fill port may be closed with a band of outer sealant. This sealant forms a permanent seal around the perimeter of the sample (see Figure 1). It may be made from a low molecular weight saturated hydrocarbon rubber with hydroxy terminations, which is cured, or crosslinked, by mixing with a saturated hydrocarbon diisocyanate curing agent (see "Sealant Preparation").

MANUFACTURING PROCEDURES

The preceding Laboratory Procedures are intended to be an accurate model of a complete manufacturing process. Where materials, equipment, procedures, or conditions for manufacturing are not specified in this section, it may be assumed that the analogous item in the Laboratory Procedures section applies. This process consists of the following Manufacturing Steps:

1. Cut and seam glass.

2. Wash, acid etch, rinse, and dry glass. The wash and etch can be combined by mixing a compatible soap with the hydrochloric acid.

3. Spray on silane. The spray booth must be explosion proof due to the methyl alcohol solvent for the silane. The flammable, toxic fumes from the ventilated booth can be removed with a water spray or may be incinerated.

4. Oven cure silane. To save oven space, the glass sheets may be stacked with a space between them for circulating hot air. The oven may be humidified to help bond the silane to the glass.

It may be necessary to grind off the silane coating at the edges of the glass cover sheets, where the inner and the outer seals must adhere to the glass. However, accelerated aging of laboratory samples indicate that this Step is not necessary.

5. There are two alternate procedures for forming the first, or inner, seal between the two sheets of glass (see Figure 1). The first procedure is to use an approximately 1/2 inch wide by 1 to 3 millimeter thick, 2-sided tape or free-standing adhesive tape, such as Isotack made by 3M. The tape may be applied to the glass either from a hand held dispenser or with automated machinery. A second method of forming the first seal is to extrude a bead of hot melt adhesive along the edges of one of the sheets of glass. Next, the second sheet of glass is placed on top of the hot melt adhesive on the first sheet of glass. This sandwich is then placed in a hot press which simultaneously softens the hot melt adhesive and presses the two sheets of glass together, thus bonding the two sheets of glass together, and affixing the spacing between the two sheets of glass precisely. Fill and vent ports may be made by omitting the sealant or tape in the appropriate places.

6. The above sandwich may be formed rapidly and simply by using what is called a "butterfly" table, which has a hinge down the middle of its flat surface. The sheet of glass with the tape or the extruded hot melt adhesive is placed on one side of the hinge. One the other side of the hinge is placed the second sheet of glass. Then the horizontal surfaces of the table on either side of the hinge are swung up to the vertical position, each half carrying its sheet of glass with it. The sandwich is formed when the two halves of the table hinge to a vertical position. Alternately, all of the preceding steps may be done with the glass being vertical, rather than horizontal, thus obviating the need for a butterfly table.

7. The sandwich is cooled to 5 to 10° C. A chamber with circulating cold air may be used. Inside this cooling chamber is a tilt table on which the glass/cavity/glass sandwich is placed during its cooling, filling and, optionally, during its polymerization, or gelling. The dispenser of the mixed A, B and C solutions, housed in a ventilated glove box, may also be inside this cooling chamber. The dispenser needle(s) or die(s) may be inserted into the side of the sandwich by hand.

8. Simultaneously with Step 7, the sandwich cavity is flushed with an inert gas.

9. The cavity of the sandwich is next filled with the monomer solution consisting of parts A, B, and C mixed together homogeneously, and, if possible, precooled to 5 to 10° C.

Unlike the Laboratory Procedure, which uses a 2 component hand-held syringe, for Manufacturing a meter/mix pump is used. This may be a 3 component meter/mix with the ratios for A, B, and C being 4:1:1. 3 components are used instead of 2 because a solution containing both the monomer and either of the 2 catalyst parts has a short shelf life. Component A consists of an aqueous solution of all of the ingredients except the 2 redox catalyst components. Part B may consist of an aqueous solution of sodium metabisulphite, and part C may consist of an

aqueous solution of sodium persulphate. Part B, a reducing agent, is protected from atmospheric oxygen with inert gas bubbling and blanket. Fresh part C is prepared every 4 hours. The meter/mix also removes dissolved atmospheric oxygen from the solutions A, B, and C; with a vacuum boil and/or bubbling with an inert gas. It is preferred that the meter/mix uses gear pumps in order to maintain a precise ratio of components, which is necessary for a uniform switching temperature of the light valve sample. The meter/mix may use a dynamic mixer (preferably disposable) in addition to the static mixer in order to ensure uniform mixing. The metering function of the meter/mix stops the pumping when exactly the correct volume has been pumped to fill the cavity in the sandwich to the correct thickness. Steps 8, 9, and 10 can be controlled digitally, where the operator only inputs the glass size and the cavity thickness, inserts the die(s) and/or needle(s), and then pushes the flush and fill button.

The output of the mixer(s) is valved to a source of the inert gas which is used to flush air from the sandwich cavity. Following the flow path, the filling die(s) or needle(s) come next. The die(s) or needle(s) are inserted into the cooled, unfilled sandwich, which is first flushed with inert gas (Step 8). Then, by switching a valve, the mixed parts A, B and C are injected, which, due to the low viscosity of this mixture (approximately 20 centipoises), can fill a 1 meter by 1 meter sample in 1 minute.

During filling, the unfilled sandwich is placed on a tilt table which is inside the cooling chamber, where it is cooled to and maintained at 5 to 10° C (Step 7). The tilt table is used because tilting the sandwich so that the fill port(s) are at the bottom, and the vents are above, facilitates removing all of the gas when the cavity is being filled with the mixed parts A, B, and C, thus preventing bubble formation. The table may be tilted manually.

During filling, the filling port(s) of the sandwich and the meter/mix dispenser are contained within a ventilated glove box in order to prevent the toxic fumes from the monomer in part A from escaping. This glove box may be inside the cooling chamber. Any excess of parts A, B, or C, or water, unmixed or mixed, coming from a needle, die, or the meter/mix is toxic, and so is carefully stored and disposed of. After curing, the vent needles and injector die(s) or needle(s) and the static and dynamic mixers are removed from the sandwich edges for cleaning or disposal.

10. After the filling and the gas and bubble removal are completed, the tilt table is made horizontal so that the thickness of the mixed parts A, B and C, is uniform, for uniform reflectivity and appearance when the light valve is above its switching temperature and is opaque white. In this horizontal position, the sample is cured for 10 or more minutes at 5 to 10° C. In order to increase line speed, during cure the sandwiches may be stacked horizontally with space between them for circulating cold air to remove the heat of polymerization. This stacking is analogous to the stacking in the oven to cure the silane (Step 4). However, in this case, the stack of sandwiches must move with very little vibration or deviation from the horizontal, because these would disrupt the formation of a strong, homogeneous, and well bonded gel.

11. The second, or outer, seal is applied, either manually or with automated machinery. It may be made of the same 2 components as used for the outer seal in the Laboratory Procedure (see "Sealant Preparation"). Approximately 10% of a colloidal carbon or silica filler, with appropriate silane coupling agents, may be added to this formulation in order to make it thixotropic, so that the sandwich can be handled immediately after application of the sealant. This filler, by blocking crack propagation, also increases adhesion to the glass, elastic elongation, and yield strength. These 2 sealant components are mixed together and dispensed

using a meter/mix machine which is similar to the meter/mix used for pumping and mixing the monomer solution parts A, B and C except that: there are only 2 components for the sealant; the accuracy of the ratio is not as critical; and the viscosity of the sealant is much greater, approximately 200,000 centipoises.

Alternately, the outer seal can be made with a hot melt sealant. For this purpose, a good sealant is Delchem 2000, which is both durable and has low moisture permeability because, like the above sealant, it is a saturated hydrocarbon; and it covalently adheres and crosslinks slowly upon exposure to atmospheric moisture. An advantage of this sealant is that because it is a hot melt, it is not necessary to wait for crosslinking to occur before it is safe to handle the sample. This sealant was developed to keep water vapor out of sealed insulated windows. Hot melt sealant may be pumped to a heated application gun from a heated platen/piston pump unloader with a heated hose.

Steps 7, 9, 10, and 11 do involve a small amount of hand labor, which is acceptable, although these steps could be totally automated. Almost all of the manufacturing equipment required for the above procedures is commercially available, but is being used for other purposes. Almost all of the above Manufacturing Steps are either identical with or similar to the operations which are performed during the automated manufacture of sealed insulated windows, including Steps 1, 2, 5, 6, 8, and 11. The additional Steps and equipment are: the silane spray (3) and its oven cure (4), the cooling chamber (7) with its tilt table (10), and filling with the meter/mix (9), using a glove box. Therefore, the easiest way to build the machinery to mass produce these light valve sandwiches is to adapt, modify, and add on to existing automated machinery made for manufacturing sealed windows.

CONCLUSIONS

A rapid preparation process for light valve samples is made possible by using a low viscosity aqueous solution of a pair of molecularly designed monomers, such as for example, N substituted acrylamide monomers with low melting points, and an acrylamide crosslinking monomer, all of which, after filling the glass/cavity/glass sandwich, are polymerized with the previously added redox catalyst pair of persulfate/ metabisulphite. A coherent set of procedures, materials, equipment, and conditions for preparing light valve samples were described. These samples perform satisfactorily regarding: range of switching temperatures available, narrowness of switching temperature, opacity or reflectivity when switched off (white), light transmission with switched on (transparent), uniformity of switching temperature, minimal drift of switching temperature and absence of optical defects, haze, or yellowing after accelerated aging with: heat, water loss, or concentrated solar ultraviolet light.

The time for filling a 1 square meter glass/cavity/glass sandwich with a 2 millimeter thick cavity is 1 minute (improved by a factor of 50), and the time after filling for the monomer solution to form a gel is 10 minutes (improved by a factor of 20). Since filling and gelling were the slow steps in sample preparation, both of these improvements taken together make possible a rapid preparation process.

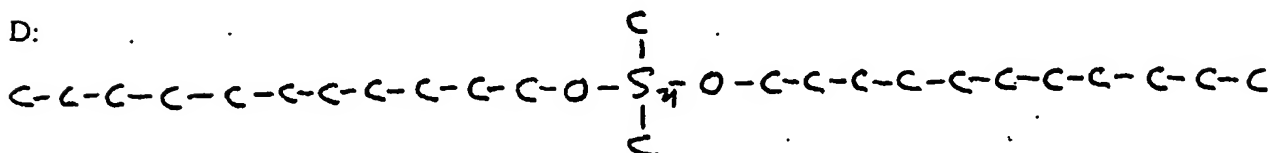
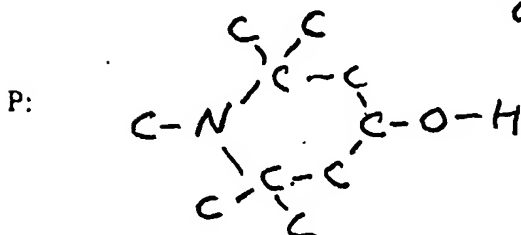
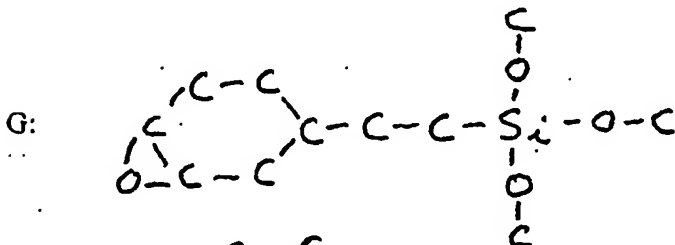
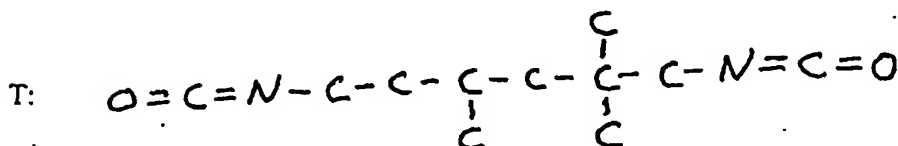
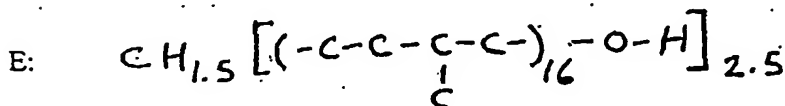
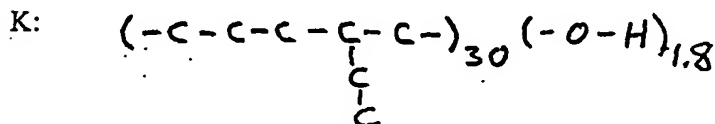
SEALANT PREPARATION

INGREDIENTS

Kraton L-2203 (K) from Shell Chemical, Poly bd Epol (E) from Mitsubishi Chemical, Vestanat TMDI trimethyl hexamethylene diisocyanate (T) from Creanova, ~~epoxy~~ cyclohexyl ethyl trimethoxy silane (G) from Gelest, pentamethyl piperidinol (P) from Aldrich, and Fomres UL-28 dimethyl tin dilaurate (D) from Witco.

MOLECULAR STRUCTURES

The ^{subscripts} structures for K and E are approximate ^{average values.} Hydrogen atoms attached to carbon atoms are not shown.



MOLECULAR DESIGN

K and E form the basic polymer backbone. They are saturated hydrocarbon chains with protruding methyl or ethyl groups and terminal hydroxy functionality. The flexible hydrocarbon backbone gives the resulting polymer a high elasticity. The saturation provides high resistance to thermal oxidation, solar ultraviolet light, hydrolysis, and water permeation. The groups protruding from the chain in somewhat random locations prevent close packing of the chains and subsequent crystallinity, thus making the cross linked sealant polymer a rubber, rather than a plastic. The hydroxy functionality allows turning both of these high viscosity liquid polymers (K and E) into a solid rubber by crosslinking them into a three dimensional net structure. The terminal location of the functionality gives rapid and complete crosslinking and greater mechanical strength. The elastic modulus and elongation of the sealant is determined by the ratio of E to K. More E, with its functionality greater than 2, gives more crosslinks, and thus less elastic elongation. K and E are relatively expensive because they are manufactured in small quantities.

T is a diisocyanate, which reacts with the hydroxy functionality of K and E to form the chain growth and crosslinks or "cure". This diisocyanate crosslinker is chosen because it reacts rapidly at room temperature and is also resistant to thermal oxidation and sunlight, because it is also based on a saturated hydrocarbon. The protruding methyl groups make it soluble in K and E and also increase the sealant's flexibility by preventing the cured isocyanate groups from associating due to their high polarity. The amount of T is 105% of stoichiometric to compensate for adsorption of and reaction with atmospheric moisture during compounding, storage, and cure, which would deactivate its isocyanate functionality. Stoichiometry is based on the total hydroxy functionality of K, E, and P. The excess T also helps adhesion. T is highly toxic, but has a low vapor pressure at 20°C, so that skin contact, but not inhalation, must be avoided.

G provides adhesion to glass because its glycidyl functionality reacts with the hydroxy functionality of K and E, and its methoxy silane functionality reacts with the hydroxy functionality on the surface of glass and stainless steel.

P is a hindered amine, which decomposes the hydrogen peroxide and ozone created by solar ultraviolet, and thus protects the sealant from solar degradation. Its hydroxy functionality reacts with T to covalently bond it into the polymer net, so it cannot be leached out over time. The methyl group on the nitrogen prevents the amine in P from reacting with T, which would destroy the peroxide decomposing ability of P.

D is a catalyst for the reaction of T with the hydroxy functionality of K, E, and P. The laurate groups give it solubility in K and E, and the methyl groups, due to their small size, make this reaction rapid and complete at room temperature.

Approximately 10% Carbon powder or flumed silica, each with appropriate silane surface treatment, may be added to improve adhesion and tear strength, but at the cost of increased viscosity.

COMPOUNDING

For a static mixer of parts A and B to work well, the ratio of A to B must not be greater than 4:1, and the viscosities of A and B must be similar. In order to minimize viscosity for ease of handling and application, a 4 parts A to 1 part B ratio with the following formulation is used:

Part A, percent by		Part B, percent by	
mol	weight	mol	weight
K 31.1	64.45	E 6.5	12.8
E 7.5	14.8	T 49.2	7.2
G 3.8	0.5		
P 1.7	0.2		
D .2	0.06		

The G, P and D components are made up as 10% solutions in K to insure that they are dispersed evenly throughout the Part A. The P requires heating K to 70°C to dissolve. For Part A the components are added sequentially with mixing in an airtight container for one hour. The part B is mixed vigorously in an airtight container for 4 hours. During the mixing of part B, the E and T react to form a relatively low viscosity prepolymer.

PERFORMANCE

The viscosity of A and B are 15,000 and 10,000 poises at 20°C. When stored in air and moisture-tight containers, the parts A and B have a shelf life of 3 months at 20°C. When used with a 4:1 syringe cartridge and a 10 element static mixer, the sealant has a working time of 10 minutes, a green strength time of 1 hour, and a cure time of 4 days, all at 20°C.

The cured sealant has very low water transmission, high resistance to thermal oxidation and sunlight, a high elongation of 1000%, low modules of elasticity (in order to minimize stress on the adhesive bond to the substrate), and good adhesion to glass and stainless steel, with cohesive rather than adhesive failure occurring after accelerated aging.

Claim 1

A light valve consisting of:
two cover layers,
at least one of which is transparent,
and an optically active layer between these cover layers,
with the optically active layer consisting of :
a polymer which may be a copolymer,
and a solvent which may be a mixture of solvents,
with the polymer reversibly precipitating from the solvent upon heating to some temperature,
thereby reversibly turning the optically active layer from transparent to opaque,
with the polymer made by polymerizing one or more monomers together in the solvent,
and with the monomer being at least 20% soluble in the solvent at a temperature far enough below
the precipitation temperature of the polymer/solvent solution that the heat of polymerization does not
raise the temperature of the solution to it's precipitation temperature.

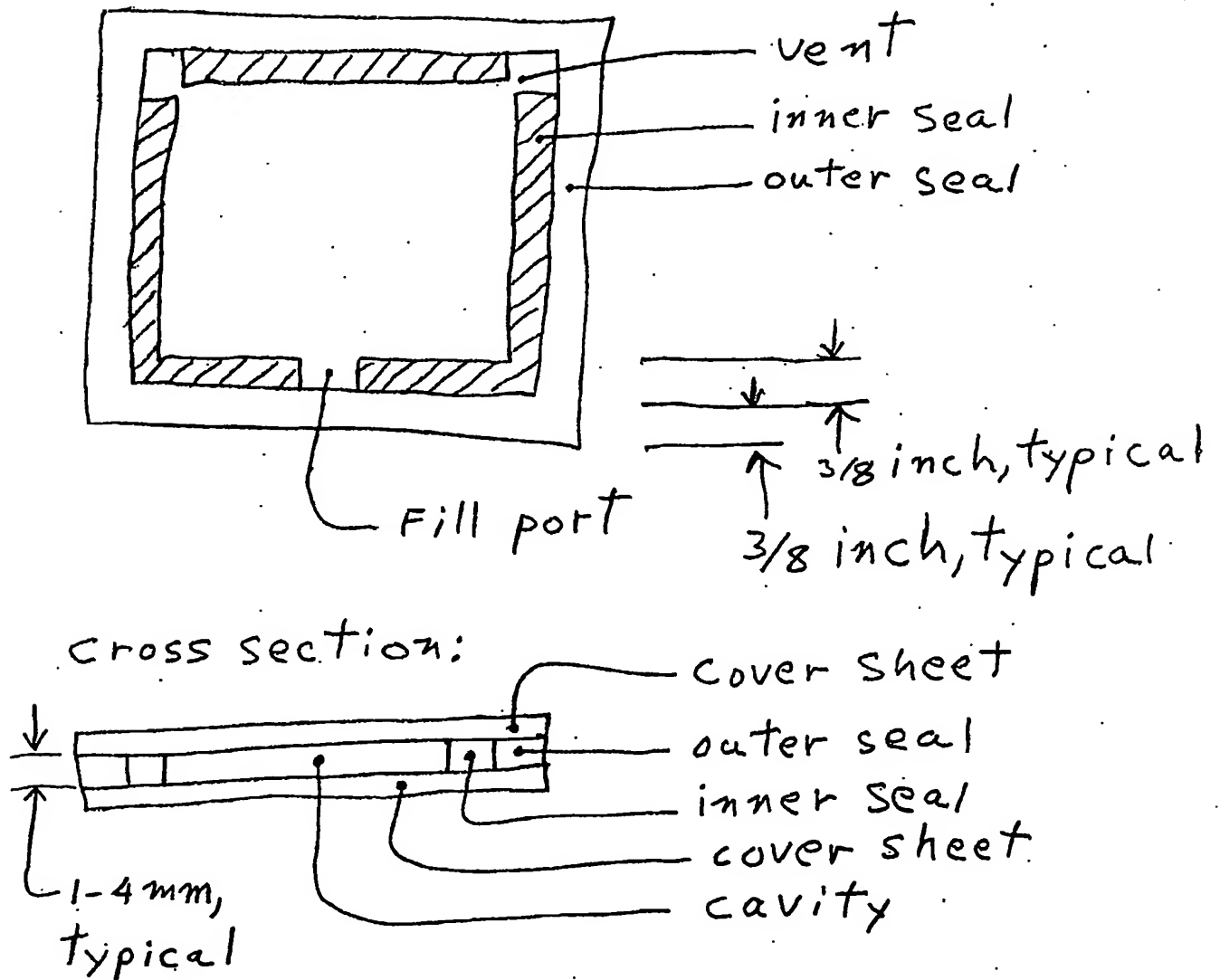
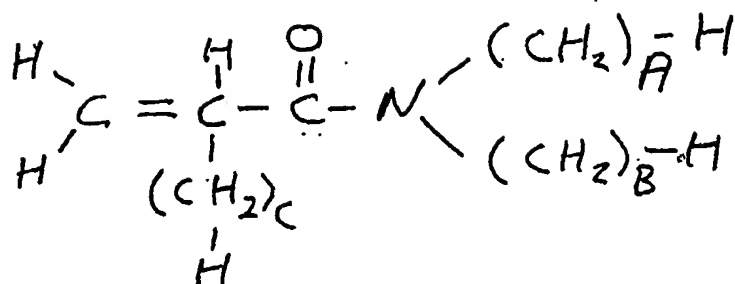


Figure 1



#	A	B	C	Acronym	A+B+C
1	2	2	0	DEA	4
2	1	1	0	DMA	2
3	4	0	0	TBA	4
4	1	1	1	DMMA	3
5	1	2	1	MEMA	4
6	2	2	1	DEMA	5
7	1	1	2	DMEA	4

Figure 2

Typical Acrylamide Monomers

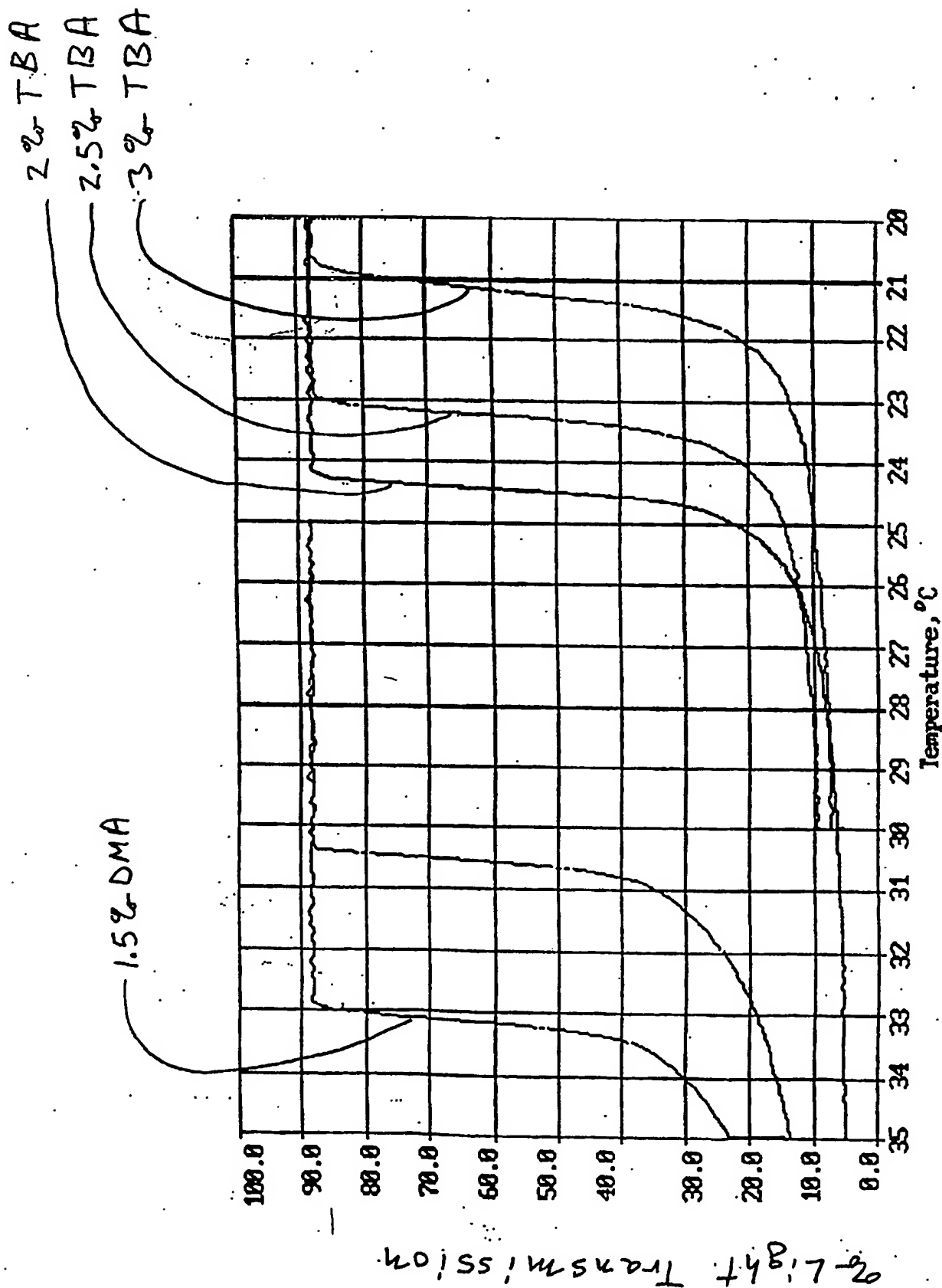
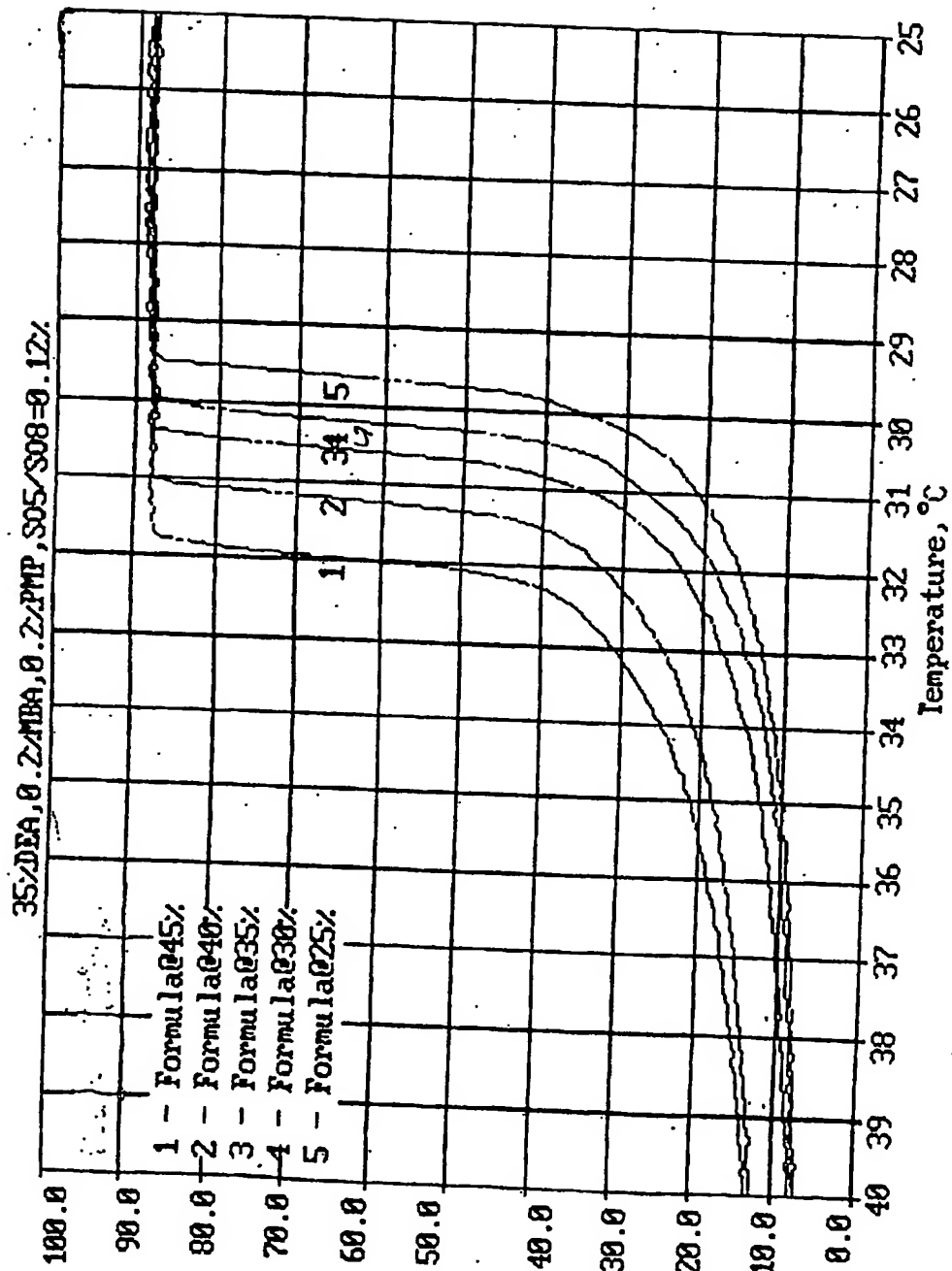


Figure 3



2. Light Transmission

Figure 4

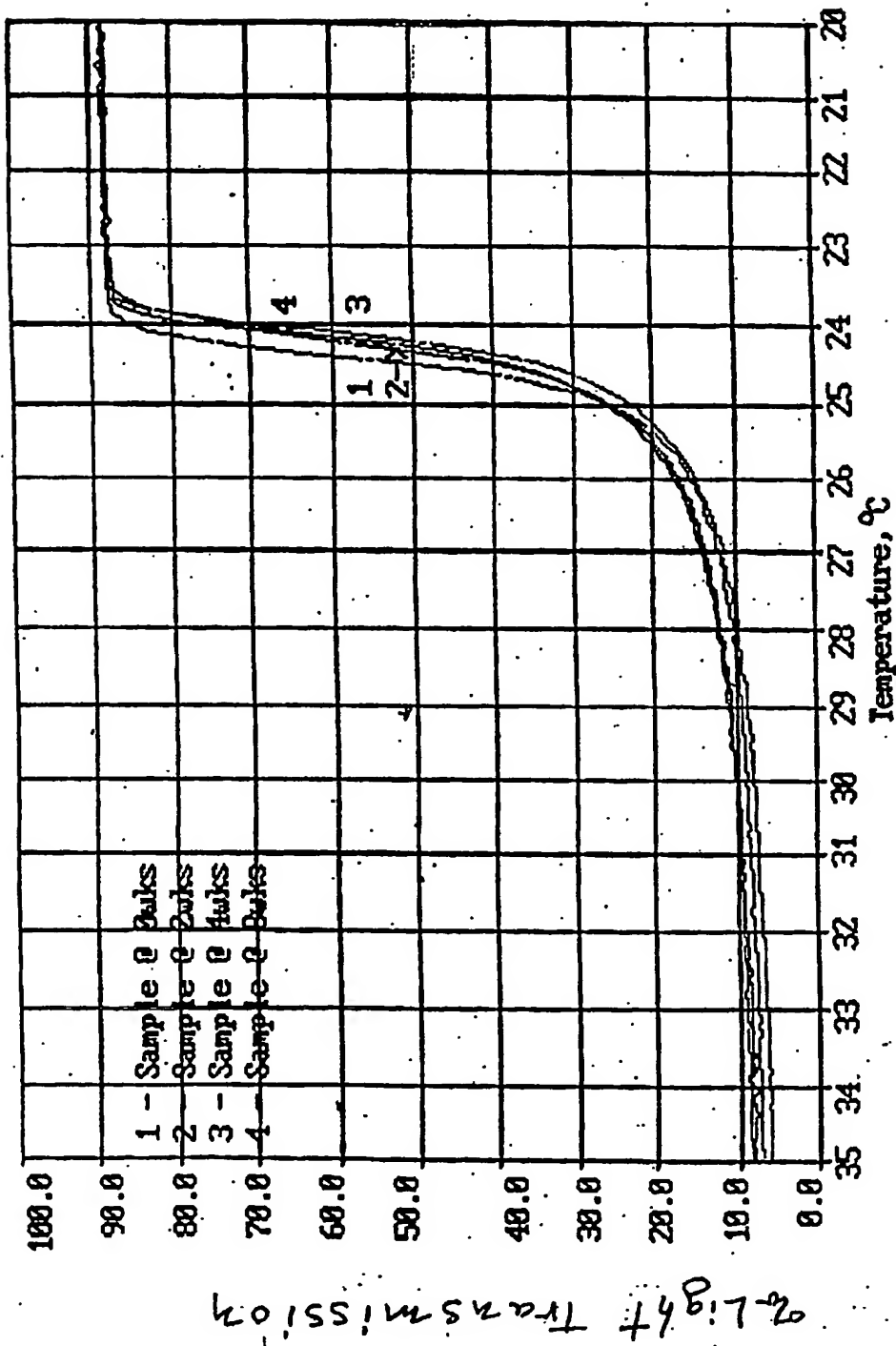


Figure 5

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